3

PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : C08F | A2

(11) International Publication Number: WO 96/26221

(43) International Publication Date: 29 August 1996 (29.08.96)

(21) International Application Number: PCT/US96/01044

(22) International Filing Date: 30 January 1996 (30.01.96)

(30) Priority Data:
08/389,719 16 February 1995 (16.02.95) US

(71) Applicant: MINNESOTA MINING AND MANUFACTURING COMPANY [US/US]; 3M Center, P.O. Box 33427, Saint Paul, MN 55133-3427 (US).

(72) Inventors: THAKKAR, Bimal, V.; P.O. Box 33427, Saint Paul, MN 55133-3427 (US). EVERAERTS, Albert, I.; P.O. Box 33427, Saint Paul, MN 55133-3427 (US).

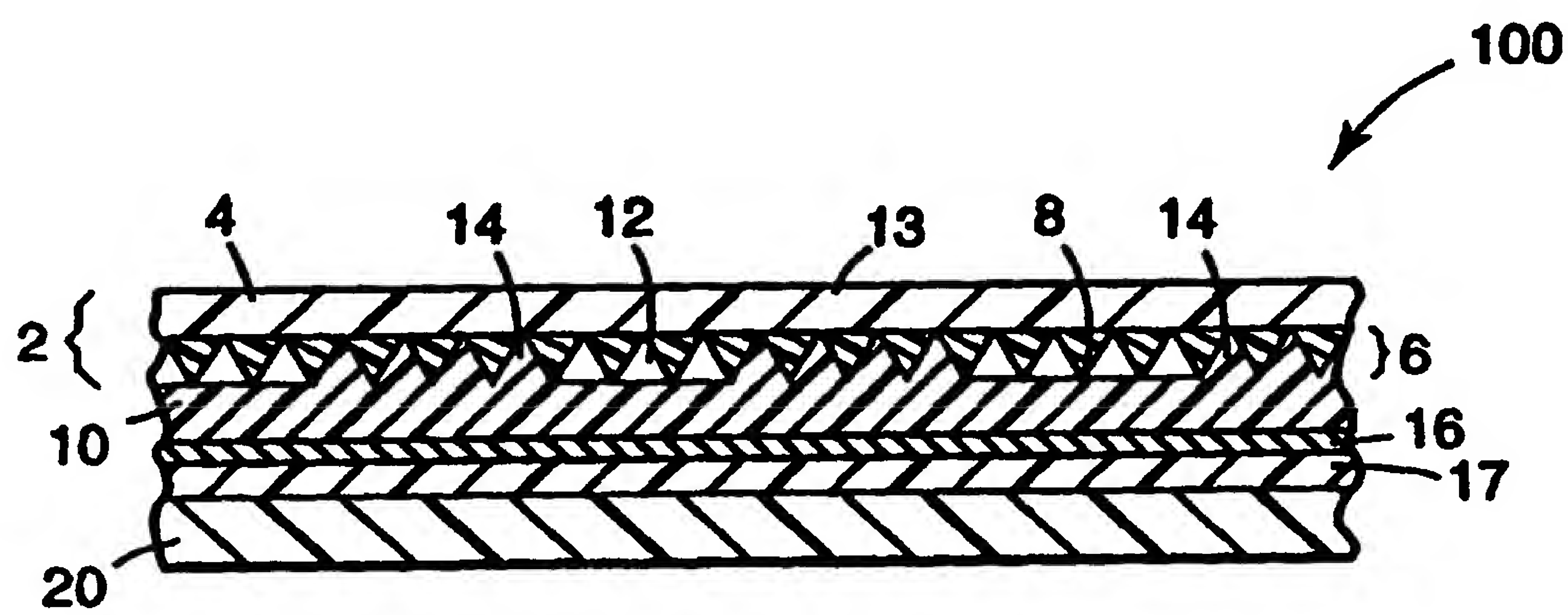
(74) Agents: JORDAN, Robert, H. et al.; Minnesota Mining and Manufacturing Company, Office of Intellectual Property Counsel, P.O. Box 33427, Saint Paul, MN 55133-3427 (US).

(81) Designated States: AL, AM, AT, AU, AZ, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AZ, BY, KG, KZ, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).

Published

Without international search report and to be republished upon receipt of that report.

(54) Title: ARTICLES INCORPORATING PRESSURE-SENSITIVE ADHESIVES HAVING IMPROVED ADHESION TO PLASTICIZED POLYVINYL CHLORIDE



(57) Abstract

The present invention provides articles comprising a substrate, preferably a retroreflective sheeting, having a coating of a pressure-sensitive adhesive composition, and further to articles wherein the adhesive adheres the substrate to a highly monomericly plasticized PVC component, preferably a PVC coated fabric. The adhesive comprises a cross-linked copolymer of a first monofunctional acrylate ester f a non-tertiary alcohol having as a homopolymer a glass transition temperature of less than -25 °C, a nitrogen containing moderately basic monomer copolymerizable therewith selected from the group consisting of N,N-dialkyl substituted amides, an optional copolymerizable acidic monomer, an optional second monofunctional acrylate ester of a non-tertiary alcohol having as a homopolymer a glass transition temperature of -25 °C or greater, and a cross-linking agent. The invention also concerns a method of bonding a highly monomericly plasticized PVC component to a substrate, preferably a retroreflective sheeting, using the adhesive.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgystan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic			SE	Sweden
CG	Congo	KR	Republic of Korea	SG	Singapore
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LR	Liberia	SZ	Swaziland
CS	Czechoslovakia	LT	Lithuania	TD	Chad
CZ	Czech Republic	LU	Luxembourg	TG	Togo
DE	Germany	LV	Latvia	TJ	Tajikistan
DK	Denmark	MC	Monaco	TT	Trinidad and Tobago
EE	Estonia	MD	Republic of Moldova	UA	Ukraine
ES	Spain	MG	Madagascar	UG	Uganda
FI	Finland	ML	Mali	US	United States of America
FR	France	MN	Mongolia	UZ	Uzbekistan
GA	Gabon	MR	Mauritania	VN	Viet Nam

ARTICLES INCORPORATING PRESSURE-SENSITIVE ADHESIVES HAVING IMPROVED ADHESION TO PLASTICIZED POLYVINYL CHLORIDE

Background of the Invention

1. Field of the Invention

The present invention relates generally to signage articles such as retroreflective and non-retroreflective articles. More particularly, the invention relates to pressure-sensitive adhesives which allow excellent adhesion of retroreflective and non-retroreflective base substrates to surfaces such as highly monomericly plasticized polyvinyl chloride coated fabric, as may frequently be used in tarpaulins.

2. Related Art

In the article "Truck Cover Market Report", DataTextile, May 1991, distinction is made between tarpaulins and truck covers. A truck cover is defined as a fitted cover or a cover specifically designed for use on a flat bed, open top, dump truck or trailer, and differs strictly from a tarpaulin per se, since tarpaulins are not usually fitted for any particular use. For the purpose of the present invention, the terms are interchangeable.

As discussed in Patent Cooperation Treaty (PCT) Application No. WO 93/10985, published June 10, 1993, tarpaulins usually consist of a fabric coated with a plastic material. The fabric, although not required in all instances, is usually a woven polyester or nylon, which may have a weft insertion. The plastic material is typically chosen to be tough and flexible, and thus plasticized polyvinyl chloride (PVC), polyamides (such as nylon and aramid), and polyprenes (such as chloroprene rubber) are commonly employed. Tarpaulins are used for many cover purposes, e.g., within the building industry, and in particular for covering trucks. They are also used for making larger tents, e.g., for use in temporary military quarters and refugee camps as well as for public events.

As further stated in th above-mentioned PCT applicati n, it is common practice to print logos, company names, slogans, instructions and other decorations on truck tarpaulins, for informative and for advertising purposes. Reflecting decorations are particularly advantageous, making the trucks visible at night.

One solution to the problem is described in the above-mentioned PCT application, which describes a tarpaulin comprising a fabric coated with a plastic material, preferably PVC, polyamide, or polyprene, provided with a decoration of a reflecting material by anchoring (with an overlaying transparent flexible film) a reflecting sheet to a piece of intermediate tarpaulin cloth, whose coating is of the same type as (or is compatible with) that of the tarpaulin, by high frequency welding or heat application, and then applying the piece of intermediate tarpaulin cloth provided with reflecting sheet and overlaying transparent flexible film, optionally formed in the desired shape, to the tarpaulin by hot air fusion.

PVC coated fabrics differ primarily in the type and amount of plasticizer added to the PVC. One commercially available PVC coated fabric has been analyzed to contain up to 42 weight percent of low molecular weight monomeric plasticizer. These low molecular weight monomeric plasticizers tend to migrate to the surface of the PVC coated fabric, and tend to cause problems in adhering materials to the PVC coated fabric with pressure-sensitive adhesives (PSAs).

Acrylic PSAs generally comprise a primary component of acrylate or methacrylate monomer or a combination of such monomers which, when polymerized, have a low glass transition temperature (T_g) and low modulus (i.e. they are rubbery and soft). These soft, tacky low T_g monomers are typically copolymerized with a secondary component consisting of high T_g monomers, usually polar monomers such as acrylic acid, methacrylic acid, itaconic acid, acrylamide, methacrylamide, and mixtures thereof. As described in U.S. Patent No. Re 24,906 (Ulrich), when such polar monomers are incorporated with a predominance of low T_g monomers, a sufficiently tacky pressure-sensitive adhesive is formed having high cohesive or internal strength. Further increase in

internal or cohesive strength (i.e., shear strength), which is often required to resist the severe environmental and chemical conditions found in transportation applications, can be obtained via crosslinking.

One approach to reducing the tendency of monomeric plasticizers from migrating out of highly monomericly plasticized PVC coated fabric and into the attached PSA is to load the adhesive with plasticizer, thereby reducing the mass transfer gradient for plasticizer migration from the PVC into the adhesive. Such an approach was taken in U.S. Patent No. 4,946,742 (Landin), which discloses normally tacky and pressure-sensitive adhesives having excellent long-term adhesion to plasticized vinyl surfaces, prepared from a representative blend of dioctyl phthalate plasticizer and a terpolymer of an alkyl acrylate, a nitrogen containing vinyl monomer and a vinyl carboxylic acid. Addition of the plasticizer to the adhesive, however, adds to the cost of the adhesive, and requires an additional process step. Furthermore, if the plasticizer present in the PVC coated fabric is different from the plasticizer present in the adhesive, a driving force still exists for the plasticizer present in the PVC coated fabric to migrate into the adhesive due to the concentration gradient.

Development of a non-plasticized PSA would allow all fabricators to apply cube-corner type and other types of retroreflective sheeting onto monomericly plasticized PVC coated fabrics, thereby reducing or eliminating the need for thermal attachment methods and for plasticized PSAs.

European Patent Application No. 615 983 A2, published September 21, 1994, describes a PSA having outstanding ability to bond to solid acidic surfaces such as acidic acid-rain resistant automotive paints and PVC, and to remain firmly bonded thereto, comprising (a) about 60 to about 90 parts by weight of at least one monomer selected from the group consisting of monofunctional unsaturated (meth)acrylate esters of non-tertiary alkyl alcohols, and mixtures thereof, the alkyl groups of which comprise from about 4 to about 12 carbon atoms which as homopolymers have glass transition temperatures below about -20°C; (b) correspondingly, about 40 to about 10 parts by weight of a basic monomer copolymerizable with the monomer of element (a); (c) about 0 to about

3 parts by weight of an acidic monomer copolymerizable with th monomers f elements (a) and (b) wherein when the acidic monomer is included, the basic copolymerizable monomer should be present in a molar excess; and (d) about 0.05 to about 1 percent by weight of a crosslinking agent based upon the total weight of (a) plus (b) plus (c). Representative examples of copolymers described therein are copolymers of isooctyl acrylate (low Tg monomer), acrylic acid and a basic copolymerizable monomer which may be selected from strongly basic, moderately basic, and weakly basic monomers. Although this work is impressive, there was not disclosed or suggested the use of the PSA compositions therein disclosed in binding a variety of materials, such as used in reflective and non-reflective signage articles, to highly monomericly plasticized PVC surfaces.

PCT Application No. WO 94/19711, published September 1, 1994, describes a retroreflective structure in which an array of free-standing retroreflective prisms is formed on a substrate for application of the structure to pre-existing substrates formed of compatible fabrics, such as tarpaulins. The structure employs a non-pressure-sensitive adhesive which requires time to cure, such as a one component moisture-curable polyurethane adhesive, to adhere the free-standing prisms to the substrate, and thus the structure requires preassembly.

It would be advantageous if pressure-sensitive adhesives lacking plasticizer could be used to adhere retroreflective and non-retroreflective sheeting to highly monomericly plasticized PVC surfaces.

Summary of the Invention

In accordance with the present invention, articles are presented which utilizes a select class of acrylate adhesives, some of which were disclosed in assignee's previously mentioned published European application, to adhere a variety of materials (such as sealing films of cube-corner retroreflective sheeting, wherein the sealing film is made using any of a variety of polymeric materials, for example polyurethane, polyester, and polyvinylchloride films, and/or directly to cube-corners made of acrylic or polycarbonate polymers, or metallized cube-corners, or other types of retroreflective sheetings (such as beaded sheetings) and

non-reflective base sheetings) to a highly monomericly plasticized polyvinylchloride (PVC) component, with sufficient peel strength, static shear strength and tolerance to plasticizer and moisture to pass at least three, preferably all tests demanded of such signage articles. As used herein the term PVC component includes PVC coated fabrics and PVC articles devoid of fabric. Particularly preferred highly monomericly plasticized PVC components are PVC coated fabrics.

In particular, one aspect of the invention is an article comprising:

(a) a layer of pressure-sensitive adhesive comprising a crosslinked copolymer of 100 parts by weight monomer of elements (i), (ii), (iii) and optionally (iv) wherein the copolymer comprises:

(i) about 50 to about 90 parts by weight (more preferably about 60 to about 80 parts by weight) of at least one monomer selected from the group consisting of a first monofunctional acrylate ester of a non-tertiary alkyl alcohol, and mixtures thereof, the alkyl group of which comprises from about 4 to about 12 carbon atoms, which as a homopolymer has a glass transition temperature less than -25°C;

(ii) about 10 to about 25 parts by weight (more preferably about 14 to about 20 parts by weight) of a moderately basic, copolymerizable (i.e. containing one ethylenically unsaturated group) monomer selected from the group consisting of N,N-dialkyl substituted amides (the moderately basic copolymerizable N, N-dialkyl substituted amide preferably selected from N-vinyl pyrrolidone, N-vinyl caprolactam, and monomers within the general formula (I):

$$\begin{array}{c} \quad\ \mathrm{R} \\ \quad\ | \\ \mathrm{CH_2{=}C{-}Z} \end{array} \qquad (\mathrm{I})$$

wherein:

R is selected from the group consisting of -H and $-CH_3$;

Z is -C (=O)NR^{1}R^2;

R^1 and R^2 are independently selected from the group consisting of alkyl groups having from 1 to 10 carbon atoms);

(iii) about 0 to about 7 parts by weight (more preferably from about 3 to about 6 parts by weight) of an acidic monomer copolymerizable with the monomers of elements (i) and (ii) wherein when the acidic monomer is included, the basic copolymerizable monomer is present in a molar excess;

(iv) 0 to about 30 parts by weight of a second monofunctional acrylate ester of a non-tertiary alcohol having as a homopolymer a glass transition temperature equal to or greater than -25°C; and

(v) about 0.01 to about 1 percent by weight of a crosslinking agent based upon the total weight of (i) plus (ii) plus (iii) plus (iv), wherein the relative amounts of the monomers are selected such that the article passes at least three (preferably four, most preferably all) tests selected from the group consisting of a pressure wash test after water soaking, a pressure wash test after thermal conditioning, a static shear test (initial) and after thermal conditioning, a T-peel test (initial), a T-peel test after thermal conditioning, and a T-peel test after water soaking (these tests being more fully described herein); and

(b) the layer of adhesive coated onto a substrate.

Preferably the adhesive is used to adhere a highly monomericly plasticized PVC component, preferably a PVC coated fabric, to the substrate.

The substrate layer is preferably selected from the group consisting of i) a sealing film (preferably polyurethane, polyester, polyvinylchloride or polycarbonate) attached to a transparent retroreflective sheeting having a substantially flat surface and a structured second surface, the structured second surface comprised of a plurality of grooves defining a plurality of peaks, ii) a metallized retroreflective sheeting having a substantially flat surface and structured second surface, the structured surface having a layer of metal thereon, iii) the non-light-impinging surface of a beaded retroreflective sheeting (i.e.,

retroreflective sheetings comprising a plurality of transparent microbeads), and iv) other non-retroreflective substrates, such as polymeric films including polyurethane films, poly lefin films, and plasticized vinyl films (such as described in U.S. Patent No. 4,605,592 (Paquette et al.)) or soft metallic films such as aluminum.

In one retroreflective article embodiment of the invention, the article may be attached to a PVC coated fabric using thermal methods, such as high frequency welding, hot air fusion, and the like. This is useful when it is desired to add retroreflective sheeting to used or old tarpaulins, or when repairing torn or worn tarpaulins.

Another aspect of the invention is a method of bonding a highly monomericly plasticized PVC component to a substrate, the method comprising the steps of:

(a) formulating an adhesive composition as described in reference to the inventive signage article;

(b) applying the adhesive composition either to a highly monomericly plasticized PVC component, an attachment surface (i.e. a surface opposite the non-reflective surface) of a substrate, or both; and

(c) joining the surface of the substrate with the PVC component, the adhesive composition positioned between the PVC component and the attachment surface of the substrate, wherein the attachment surface of the substrate is defined by previously mentioned substrates.

One great advantage of the method of the invention, particularly when retroreflective substrates are to be adhered to truck tarpaulins as conspicuity markings, is that the user can easily apply the retroreflective sheeting to the tarpaulin without any additional tools, such as high frequency welding and hot air fusion machines.

Further aspects and advantages of the invention will become apparent from the following description of the invention.

Brief Descripti n of the Drawing

FIG. 1 is a cross-sectional view (enlarged) of an illustrative article of the invention, comprising the cube-corner retroreflective article adhered to a PVC component using an adhesive as described herein;

FIG. 2 is a cross-sectional view (enlarged) of an illustrative article of the invention, comprising the metallized layer of a cube-corner retroreflective article of adhered to a PVC component using an adhesive in accordance with the invention; and

FIG. 3 is a cross-sectional view (enlarged) of an illustrative article of the invention comprising an embedded lens retroreflective substrate adhered to a PVC component using an adhesive in accordance with the invention.

These figures are not to scale and are intended to be illustrative and non-limiting.

Description of Illustrative Embodiments

The invention provides a retroreflective article comprising a highly monomericly plasticized PVC component adhered to a substrate by a pressure-sensitive adhesive (PSA). The articles of the invention, by virtue primarily of the adhesive, pass at least three rigorous tests, and preferably all tests, further described herein, which are used to determine if the articles will withstand static shear after water soaking, static shear after thermal conditioning, pressure washing, and the like, in a real world setting. Many previously known adhesives have not shown the ability to meet at least three of these tests. Before discussing these tests and the pressure-sensitive adhesives, however, the inventive articles are described with reference to the drawing figures.

Retroreflective Articles

A. Articles incorporating Cube-corner Retroreflective Sheeting

One preferred embodiment of the articles of the present invention relates to a retroreflective article comprising a transparent retroreflective sheeting having a substantially flat first surface and a structured second surface, the structured second

surface comprised f a plurality f sets f grooves defining a plurality f peaks (in typical cube-corner sheeting at least three sets of parallel grooves intersect, whereas in prism films a singl set f parallel grooves is typical), a sealing film layer (col red or colorless) disposed in and bonded to a first portion of the grooves, a second portion of the grooves precluded from contact with the sealing film layer, and a pressure-sensitive adhesive layer (as herein described) disposed between the sealing film layer and a highly monomericly plasticized PVC component.

As used herein the term "peak" means a projection having at least two planar facets, such as prisms, pyramidal protrusions, cube-corner protrusions, and the like. The phrase does not include protrusions which do not include planar facets, such as protrusions present in holographic films.

The term "transparent retroreflective sheeting" means a plastic sheeting transmitting at least 90% of incident light in the visible spectrum (about 400 to 700 nanometers wave length), as determined by a standard spectrophotometer.

Referring now to the Figures, wherein like numerals are used to denote like elements from figure to figure, a preferred embodiment of a cube-corner transparent retroreflective article of the invention is illustrated in cross-section (enlarged) in FIG. 1. In FIG. 1, sheeting 100 comprises a transparent layer 2 having a flat, smooth surface 4 and a structured surface 6 comprised of a plurality of peaks 8. Layer 2 may be extremely thin to enhance flexibility, or overlay 13 may have a low modulus as disclosed in Assignee's copending Patent Application Serial No. 08/326,696, filed October 20, 1994. In that application, layer 2 is formed from a thermoplastic overlay film 13 and decoupled thermoset cube corner elements.

A thermoplastic sealing film layer 10 is disposed on peaks 8, and a plurality of air spaces 12 are defined between cube-corners and sealing film layer 10 so as to impart retroreflectivity to the article. Sealing film layer 10 is adhered to layer 2 at a plurality of sealing areas 14, where the thermoplastic sealing film material has flowed between individual cube corner elements to reach and fuse with the thermoplastic overlay film 13. The sealing prevents water, oil and the like from entering between sealing film layer 10 and layer 2.

In FIG.1, reference numeral 16 denotes an opti nal chemical primer layer r a cor na treatment layer positioned between sealing film layer 10 and a PSA layer 17. Chemical and/ r physical priming is preferred but not necessary t the invention. The combination of layers consisting of layer 2, sealing film layer 10, and primer layer or corona treatment layer 16 is designated as a retroreflective sheeting substrate 18. A liner (not illustrated) is preferably positioned on the surface of PSA layer 17 so as to protect its surface prior to adhering to a highly monomericly plasticized PVC component 20.

FIG. 2 illustrates another inventive article embodiment, respectively. FIG. 2 illustrates a cube-corner retroreflective sheeting 200, comprising layer 2 as in the embodiment illustrated in FIG. 1. However, embodiment 200 comprises a metal layer 3, which serves to reflect light incident upon layer 2. No sealing layer is present. FIG. 2 illustrates a layer of PSA 17 adhering a plasticized PVC component 20 to metal layer 3. This embodiment eliminates the need for a sealing film, but requires the PSA to be able to bond a plasticized PVC component to a metal surface.

Layer 2 may be any one of the cube-corner or substantially totally internal reflecting sheetings described in U.S. Patent Nos. 3,140,340; 3,648,348; 4,576,850; 4,588,258; 4,775,219; 4,801,193; 4,805,984; 4,895,428; 4,906,070; 4,938,563; 5,056,892; 5,138,488; 5,175,030; and 5,183,597.

More concretely, layer 2 preferably comprises a large number of precisely shaped elements (preferably pyramidal, cube-corners or a series of parallel prisms) defined by grooves which define the elements. The pyramids, cube-corners, or prisms substantially totally reflect the light in a direction opposite to the incident direction. The precisely shaped elements define a plurality of pockets 11 (FIGs. 1 and 2), filled with air or other fluid. "Substantially totally internal reflecting" pertains to the optical quality of the film, and means that the film has a T-Test Value of 5% or less, wherein the T-Test is described as follows. The optical quality of a retroreflective film can be evaluated with apparatus including a laser (such as a Spectra-Physics Inc. Model 117A) with a spatial filter, a beam expander, and a collimator. Two diaphragms or irises are placed 18 and 38 cm from the laser, and

an annular sample holder with an opening 6.35 cm in diameter is placed 84 cm from the laser. Directly behind the sample holder is an int grating sphere (with a 3 cm diameter aperture) and a LABSPHERE ML-400 radi meter. Using the diaphragms or irises, the laser is focused through the aperture to obtain a clean circle of light of about 3 mm diameter on a black surface mounted on the sample holder. A source intensity measurement of 100% is taken with no sample in place. The TIRF to be tested is then mounted on the sample holder with its flat surface facing the laser and its grooves extending vertically. Unless otherwise reported, T-Test Values are measured at ambient temperature. Readings are then made at from 12 to 15 different points on the TIRF within a 5 cm diameter area while making sure that none of the light strikes the frame of the sample holder. The readings are averaged and multiplied by 100 to give percent transmission which is the T-Test Value of the TIRF sample. T-Test Value is a criterion of the fidelity of replication of the TIRF. Smaller T-Test Value percentages indicate better fidelity of replication than larger percentages, and a T-Test Value of 5% or less indicates that the film is substantially totally internal reflecting.

Layer 2 preferably comprises an acrylic material having excellent durability, such as poly(methyl)methacrylate, polyester (such as polyethylene terephthalate), polyamide, polycarbonate, poly(vinylchloride), poly(vinylidenechloride), cellulose acetate butyrate, cellulose acetate propionate, poly(ethersulfone), polyurethane, ionomer resins (such as the metal ion crosslinked polyethylene/acrylic acid ionomers known under the trade designation SURLYN), and the like, and preferably also comprises a UV absorber.

From the aspects of mechanical strength and light reflectivity, layer 2 preferably has a refractive index of about 1.6, which is possible if the layer is made of a polycarbonate resin, an ionomer resin such as just described, or an acrylic resin.

Structured sheeting or layer 2 may be made as one integral material, e.g., by embossing a preformed sheet with a described array of cube-corner elements, or casting a fluid material into a mold; or they may be made as a layered product, e.g., by casting the elements against a preformed film as taught in U.S. Patent No. 3,684,348, or by laminating a preformed film over the front face of individual

molded elements. Polycarbonates and i nomers are preferred integral sheet materials.

The thickness f layer 2 preferably ranges from about 50 t about 500 micrometers in terms of the height from the apex of the pyramid or prism to the base of the base portion. If the thickness is less than 50 micrometers, the mechanical strength is not sufficient and a predetermined height is difficult to obtain for the pyramids or prisms, so that retroreflectivity decreases. If the thickness exceeds 500 micrometers, on the other hand, the total thickness of the retroreflective sheet becomes so thick that handling becomes difficult and the amount of adhesive required increases.

In the present invention, sealing film layer 10 (FIG. 1) is involved in exhibition of retroreflectivity by forming an air layer 12 between sealing film layer 10 and layer 2. In other words, in order for layer 2 to exhibit retroreflectivity, an air layer must exist below the precisely shaped elements so as to produce a change in refractive index. Sealing film layer 10 is laminated onto the structured surface of layer 2, and sealing film layer 10 is bonded thereto with heat and/or radiation at a plurality of locations, thus forming a plurality of sealed air pockets. It is understood that "air" is used only as an example and that other fluids may be used, depending on the atmosphere in which the articles of the invention are produced, and provided that the fluid used is significantly different in refractive index from layer 2 (a difference in refractive indices of 0.5 is preferred). The procedures of U.S. Patent No. 4,025,159 may be used to effect the bonding of sealing film layer 3 to the structured second surface of layer 2.

If water, oil or the like enters between layer 2 and sealing film layer 10, the refractive index changes and retroreflectivity is lowered. Accordingly, the sealing film layer has the seal effect for water and the like.

Sealing film layer 10 is preferably a plastic film-like article comprising a plastic resin, such as polyurethane, polyester, polyvinylchoride and the like, which may contain a predetermined amount of one or more pigments such as titanium dioxide (white), silica, red oxide, and the like, added to the resin. Particularly,

white is suitable for the present invention because recognizability of the retroreflective articles f the invention is high.

B. Articles Employing Beaded Retroreflective Sheeting

FIG. 3 is a cross-sectional view (enlarged) of an illustrative article embodiment 300 of the invention comprising an embedded lens retroreflective substrate adhered to a PVC component using an adhesive in accordance with the invention. In this embodiment, the retroreflective sheeting substrate comprises a polyvinyl butyral layer 32 in which a plurality of glass microspheres 34 are embedded. Other organic layers, such as glyptal, alkyd, ethylene and/or propylene acrylic acid copolymers, ethylene methacrylic acid copolymer, ionomers, crosslinked and /or uncrosslinked aliphatic polyurethanes, vinyl, PMMA, and the like may also comprise layer 32. A cover material 38 is illustrated over printed indicia for abrasion resistance, chemical deterioration resistance, and the like, which would be desired by users of the inventive articles in prolonged (i.e. greater than 1 year) outdoor usage, such as license plates, highway signs, street signs, and the like. A reflective layer 36, PSA layer 40, and plasticized PVC component 42 complete the structure.

Preferred embedded lens retroreflective substrate sheetings include those known under the trade designation SCOTCHLITE, particularly the 3700, 4200, and 5300 series, available from Minnesota Mining and Manufacturing Co., St. Paul, MN, hereinafter 3M). Enclosed-lens retroreflective sheetings may also be used and illustrative examples are described in U.S. Patent Nos. 2,407,680, 4,664,966 and 4,511,210. Also useful retroreflective substrates are encapsulated-lens sheetings such as are disclosed in U.S. Patent Nos. 3,190,178; 4,025,159; 4,896,943; 5,064,272; and 5,066,098. .

Non-reflective Articles

As previously mentioned, non-reflective substrates may be adhered to highly monomericly plasticized PVC components using the inventive adhesive. Illustrative examples of suitable non-reflective substrates include those previously mentioned

polymeric films including polyurethane films, polyolefin films, and plasticized vinyl films (such as described in U.S. Patent N . 4,605,592 (Paquette et al.), or soft metallic films such as aluminum. Other substrates include one attachment sheeting of a hook and loop attachment system such as those known under the trade designations VELCRO and SCOTCHMATE, the latter available from 3M.

Printed Indicia

It should be noted that the articles of the invention may have human and/or machine readable indicia, such as desired alpha-numeric indicia, bar codes, logos and the like, printed on the exposed surface of the substrate (i.e. that surface of the substrate not having adhesive attached thereto), which may subsequently be buried beneath adhesive and cover film layers, such as described in the previously incorporated by reference PCT applications. The printed indicia may be printed using wax-based binder/colorants or resin-based binder/colorant layers in a thermal mass transfer process, such as disclosed in assignee's pending United States Patent Application Serial Nos. 08/386,279_and 08/386,280, both filed February 9, 1995, and or printed using the dry toner powder procedures of U.S. Patent No. 5,085,918 and pending United States serial no. 08/335,468, filed November 7, 1994.

Primer layer

The surface of retroreflective and non-retroreflective substrates which contacts the adhesive can be a wide variety of materials. Therefore, surface treatments may be necessary to secure better adhesion to the plasticized PVC component.

Particularly preferred thermoplastic resin for forming a sealing film layer are polyester and polyurethane resins. However, bonding of polyurethane and polyester films to adhesive layers is not easy and further, when processing aids are present on the films, they tend to migrate toward the interface between the adhesive and the film, causing weakening of the bond. When the sealing film layer is primed either physically or chemically, however, these problems can effectively be overcome.

In the present inventi n, a chemical primer layer r a corona treatment layer is preferably disposed between sealing film layer 3 and PSA layer 5. When a chemical primer layer and/ r corona treatment is empl yed, inter-layer adhesion between the sealing layer film 3 and PSA layer 5 can be improved, and thus high adhesion of the articles of the invention to a substrate is possible.

Suitable chemical primer layers may be selected from urethanes, silicones, epoxy resins, vinyl acetate resins, ethyleneimines, and the like. The urethane and the silicone types are particularly effective chemical primers for polyester colored sealing film layers. Among the silicone type, the primer layer having a continuous gelled network structure of inorganic particles, which is described in Japanese Unexamined Patent Publication (Kokai) No. 2-200476, is suitable for the present invention. This is because it has particularly remarkable affinity for polyester resins and polyolefin resins. Examples of chemical primers for vinyl and polyethylene terephthalate films include crosslinked acrylic ester/acrylic acid copolymers disclosed in U.S. Patent No. 3,578,622.

The thickness of the chemical primer layer is suitably within the range of 10 to 3,000 nanometers (nm). If the thickness is less than 10 nm, the primer effect is minimal and if it exceeds 3,000 nm, on the other hand, inter-layer peel is likely to occur in the primer layer.

Corona treatment is a preferred physical priming that can be suitably applied to the unexposed surface of the substrate onto which is then coated the adhesive of the present invention. Corona treatment improves the inter-layer adhesion between the adhesive and the substrate. Corona treatment of films is a well-known technique, and is described generally in Cramm, R.H., and Bibee, D.V., The Theory and Practice of Corona Treatment for Improving Adhesion, TAPPI, Vol. 65, No. 8, pp 75-78 (August 1982), and in U.S. Defensive publication H 688, published October 3, 1989.

Pressure-sensitive Adhesives

Adhesives useful in the invention are pressure sensitive and preferably possess good initial tack (sometimes referred to as "preadhesion"), thus

providing easy application of retroreflective sheeting onto m nomericly plasticized PVC components.

The PSAs should have acceptable performance after absorption of plasticizer. During summer, the temperature on the PVC canvas side of a truck trailer could conceivably reach as high as 130° F (54°C). This would enhance the migration of the plasticizer into the adhesive.

The PSAs should have acceptable performance after exposure to water or moisture. Under rainy conditions, water could be present at the interface between the retroreflective sheeting and the PVC coated fabric material. Water would have a greater effect on the performance of the adhesive if it contained more hydrophilic components.

Further, there is preferably no uniform lifting of the retroreflective sheeting during conditions of stress, such as when attached to curtain-sided truck trailers to be opened and closed. Truck trailers would need frequent washing due to the extensive amount of time spent on the road under a wide variety of conditions. The ability of the adhesive to withstand delamination during pressure washing is important.

A. Primary Acrylic acid and meth(acrylic) acid esters

The acrylic copolymers useful in the adhesive of the invention preferably contain from about 50 to about 90 parts per hundred parts by weight monomer, more preferably about 60 to about 80 parts per hundred parts monomer, contained in the copolymer of at least one monomer selected from the group consisting of a first monofunctional acrylate or methacrylate ester of a non-tertiary alkyl alcohol, the alkyl group of which comprises from 4 to about 12 carbon atoms, and mixtures thereof. Such acrylate or methacrylate esters generally have, as homopolymers, glass transition temperatures below about -25°C. Higher amounts of this monomer relative to the other comonomers affords the PSA with higher tack at low temperature, while lower than about 50 weight percent of this monomer reduces or completely eliminates the pressure-sensitivity of the adhesive.

Preferred acrylate or methacrylate ester monomers include but are not limited to those selected from the group consisting of n-butyl acrylate (BA), n-butyl methacrylate, isobutyl acrylate, 2-methyl butyl acrylate, 2-ethylhexyl acrylate, n-octyl acrylate, isooctyl acrylate (IOA), isooctyl methacrylate, isononyl acrylate, isodecyl acrylate, and mixtures thereof.

Particularly preferred acrylates include those selected from the group consisting of isooctyl acrylate, n-butyl acrylate, 2-methyl butyl acrylate, 2-ethylhexyl acrylate, and mixtures thereof.

B. Basic Monomers

Basic copolymerizable monomers are required in the PSAs useful in the invention to enhance both the basic character and shear strength of these adhesives.

Preferred copolymerizable basic polar monomers include moderately basic N,N-dialkyl substituted amides, and monomers which behave as N,N-dialkyl substituted amides. Examples of useful moderately basic copolymerizable monomers include N,N-dimethyl acrylamide (NNDMA), N,N-dimethyl methacrylamide, N,N-diethyl acrylamide, N,N-diethyl methacrylamide, N-vinyl pyrrolidone (NVP), N-vinyl caprolactam and the like. Weakly basic copolymerizable monomers, such as N-octyl acrylamide can be used in combination with a major amount of moderately basic monomer. Strongly basic monomers (monomers having non-stericly hindered tertiary amine terminal groups) such as N,N-dimethylaminoethyl methacrylate, N,N-dimethylaminopropyl methacrylate, N,N-dimethylaminoethyl acrylate, N,N-dimethylaminopropyl acrylate, and the like, were found to be too basic when used as the sole basic monomer, actually dehydrochlorinating PVC upon aging and thereby possibly shortening the useful life of PVC coated fabric and other PVC components. If strongly basic monomers are employed, such as N,N-dimethylaminoethyl methacrylate, it is preferred that these monomers be present in a minor amount and used in conjunction with a major amount of a

moderately basic monomer. Particularly preferred are moderately basic polar monomers, alone or in combination with other basic monomers.

Preferably, PSAs useful in of the present invention comprise from about 10 to about 25 parts by weight of moderately basic copolymerizable monomer. Exemplary mechanical test results are obtained when there is present from about 14 to about 20 parts by weight moderately basic copolymerizable monomers, particularly in conjunction with about 60 to about 80 parts by weight isooctyl acrylate and/or n-butyl acrylate as the low T_g monomer, and about 3 to about 6 parts by weight acrylic acid.

Particularly preferred basic copolymerizable monomers are represented by general Formula (I). Examples of specific Z groups include but are not limited to those selected from the group consisting of $-C(=O)N(CH_3)_2$ and $-C(=O)N(C_2H_5)_2$.

The basicity of the nitrogen containing monomers utilized in the present invention is defined by their substitution. Substituents that increase the electron density on a nitrogen by field effects or resonance in the case of aromatic bases will increase the basicity of nitrogen. The higher the degree of substitution on the nitrogen by linear or branched alkyl groups, the higher the basicity of the monomer. Conversely, substituents which decrease the electron density on the nitrogen of a basic copolymerizable monomer, such as a phenyl group will reduce the basicity of the monomer.

Using these general principles, several common basic copolymerizable monomers possess the following ascending order of basicity:
Acrylamide < N-methyl acrylamide < N,N-dimethyl acrylamide
< 3-(3-pyridinyl)propyl acrylate < N,N-(dimethylamino)ethyl acrylate.

Particularly preferred copolymerizable moderately basic monomers include those selected from the group consisting of N,N-dimethyl acrylamide, N,N-dimethyl methacrylamide, N,N-diethyl acrylamide, N,N-diethyl methacrylamide, and mixtures thereof.

C. Acidic Monomers

Depending on its basicity, the amount of copolymerizable basic monomer used is from about 10 to about 25 parts per hundred parts of the final copolymer. As long as a molar excess of the copolymerizable basic monomer is maintained, low levels (typically 0 to about 7 parts by weight, more preferably from about 3 to about 6 parts by weight) of an acidic monomer such as a carboxylic acid can be used to increase the cohesive strength of the pressure-sensitive adhesive. At higher levels, this copolymerizable acidic component tends to diminish the tack of the pressure-sensitive adhesive of the present invention.

Useful copolymerizable acidic monomers include but are not limited to those selected from the group consisting of ethylenically unsaturated carboxylic acids, ethylenically unsaturated sulfonic acids, and ethylenically unsaturated phosphoric acids. Examples of such compounds include those selected from the group consisting of acrylic acid (AA), methacrylic acid, itaconic acid, fumaric acid, crotonic acid, citraconic acid and maleic acid, β-carboxyethyl acrylate, sulfoethyl methacrylate, and the like, and mixtures thereof.

D. Secondary Acrylate Monomers

As previously mentioned, PSAs useful in the invention preferably exhibit acceptable performance on water soaking, which may be problematic if hydrophilic monomers are present. Therefore, from 0 to about 30 weight percent of a hydrophobic monomer having as a homopolymer a T_g greater than -25°C, may be substituted for or partially replace hydrophilic monomers such as acrylic acid. Useful secondary acrylate monomers include isobornyl acrylate (IBA), ethyl acrylate, methyl acrylate, vinyl acetate, and the like.

E. Crosslinking Agents

The crosslinking agent is an organic compound which reacts with the other monomers by virtue of having a plurality of ethylenically unsaturated groups. These compounds are referred to as multifunctional acrylates herein. Alternatively, a crosslinking agent is a compound which can directly react with

the polymeric backbone and result in crosslinking, for example, peroxide thermal cure or benzophenone UV cure.

A crosslinking agent is present in an am unt f from about 0.05 to about 1 percent by weight in the pressure-sensitive adhesive of the present invention based upon the total weight of the monomers employed.

The crosslinking agents are selected according to the polymerization method employed. Preferred crosslinking agents for the PSAs prepared via photopolymerization on web are multifunctional acrylates such as 1,6-hexanediol diacrylate (HDDA) as well as those disclosed in U.S. Patent No. 4,379,201 (Heilmann et al.) such as trimethylolpropane triacrylate, pentaerythritol tetraacrylate, 1,2-ethylene glycol diacrylate, and 1,12-dodecanediol diacrylate.

Additional useful crosslinking agents include hydrogen abstraction type photocrosslinkers such as those based on benzophenones, acetophenones, anthraquinones, and the like. These crosslinking agents can be copolymerizable or non-copolymerizable. Examples of non-copolymerizable hydrogen abstraction crosslinking agents include benzophenone; radiation-activatable crosslinking agents such as those described in U.S. Patent No. 5,407,971 (Everaerts et al.) within the general formula

$$[X\text{-}\overset{\displaystyle O}{\overset{\|}{C}}\text{-} \qquad \text{-}(W)_a\text{-}(CH_2)_m\text{-}(Y)_a]_n\text{-}Z$$

wherein W represents -O-, -N-, or -S-, X represents CH_3- or phenyl, Y represents a ketone, ester, or amide functionality, Z represents a polyfunctional organic segment that does not contain hydrogen atoms that are more photoabstractable than hydrogen atoms of a polymer formed using the crosslinking agent; m represents an integer from 0 to 6, a represents 0 or 1, and n represents an integer of 2 or greater; and anthraquinones, while examples of copolymerizable hydrogen abstraction initiator compounds include mono-ethylenically unsaturated aromatic ketones, particularly 4-acryloxybenzophenone (ABP), as described in U.S. Patent No. 4,737,559 (Kellen et al.).

In addition, copolymerizable α-cleavage type phototinitiators can be employed, such as acrylamido-functional disubstituted acetyl aryl ketones (such as those described in assignee's U.S. Patent Application Serial N . 08/136,576, filed October 13, 1993.

In addition, combinations of multi-functional (meth)acrylates and the hydrogen abstraction type crosslinkers or copolymerizable α-cleavage type photo initiators can be used. Low intensity UV light, such as "UV black light", is sufficient to induce crosslinking in most cases; however, when hydrogen abstraction type crosslinkers are used by themselves, high intensity UV exposure (such as by a mercury lamp processor such as those available from PPG, Aetek and others) is necessary to achieve sufficient crosslinking at high line speeds.

Yet, another method for crosslinking (not necessarily requiring addition of crosslinking agents) is by exposure to an electron-beam.

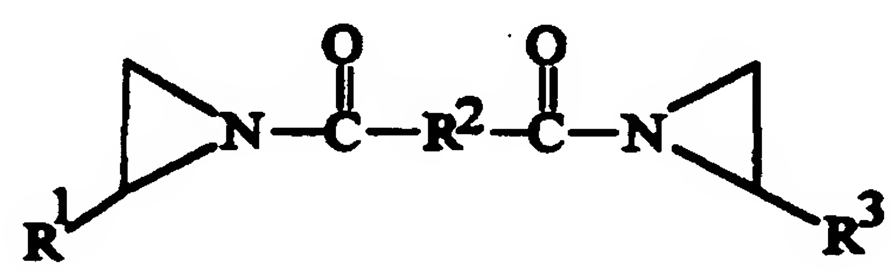
Other useful crosslinking agents include the substituted triazines, such as those disclosed in U.S. Patent Nos. 4,329,384 and 4,330,590 (Vesley), e.g., 2,4-bis(trichloromethyl)-6-p-methoxystyrene-5-triazine and the chromophore halomethyl-5-triazines.

Crosslinking agents useful in solution polymerized PSAs useful in the invention are those which are free radically copolymerizable and which effect crosslinking through exposure to radiation, moisture or heat following polymerization. Such crosslinkers include the above mentioned photoactive substituted triazines and hydrogen abstraction type photocrosslinkers. Hydrolyzable, free radically copolymerizable crosslinkers, such as mono-ethylenically unsaturated mono-, di- and trialkoxy silane compounds including but not limited to methacryloxypropyltrimethoxysilane (sold under the tradename "Silane A-174" by Union Carbide Chemicals and Plastics Co.), vinyldimethylethoxysilane, vinylmethyldiethoxysilane, vinyltriethoxysilane, vinyltrimethoxysilane, vinyltriphenoxysilane, and the like are also useful crosslinking agents.

Heat activated copolymerizable crosslinking agents, including but not limited to N-methylol acrylamide and acrylamido glycolic acid, can also be used

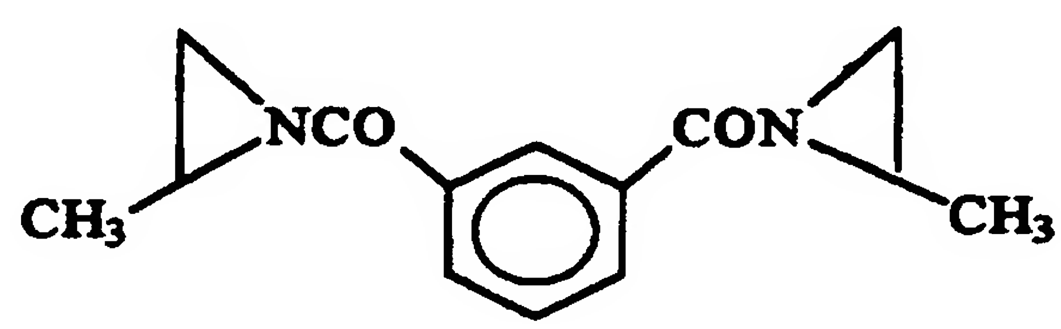
to enhance the shear strength f the pressure-sensitive adhesiv composition of the invention.

Bisamide crosslinking agents may also be employed. Bisamide crosslinking agents are more fully described as compounds within the general formula (I):



(I)

wherein R^1 and R^3 are the same or different and are independently selected from the group consisting of H and C_nH_{2n+1}, wherein n is an integer ranging from 1 to about 5, and R^2 is a divalent radical selected from the group consisting of benzeno ($-C_6H_4-$), substituted benzeno, triazine, and C_mH_{2m} , where m is an integer ranging from 1 to about 10. An example of a useful bisamide within general formula I is N,N'-bis-1,2-propyleneisophthalamide, which has the following structure (general formula II):



(II).

F. Initiators

Suitable thermal free radical initiators which may be utilized include but are not limited to those selected from the group consisting of azo compounds such as 2,2'-azobis(isobutyronitrile), hydroperoxides such as tert-butyl hydroperoxide, and peroxides such as benzoyl peroxide and cyclohexanone peroxide. Photoinitiators which are useful according to the invention include but are not limited to those selected from the group consisting of benzoin ethers such as benzoin methyl ether or benzoin isopropyl ether, substituted benzoin ethers such as anisole methyl ether, substituted acetophenones such as 2,2-

diethoxyacetophenone and 2,2-dimethoxy-2-phenyl acetophen ne, substituted alpha ketols such as 2-methyl-2-hydroxy propiophenone, aromatic sulfonyl chlorides such as 2-naphthalene sulfonyl chloride, and ph toactiv oximes such as 1-phenyl-1,1-propanedione-2-(0-ethoxycarbonyl)-oxime. For both thermal and radiation induced polymerizations, an initiator is present in an amount of about 0.01 to about 0.5 percent by weight based upon the total weight of the monomers of the instant pressure-sensitive adhesive compositions.

G. Glass transition temperature

The glass transition temperature (T_g) of adhesives useful in the present invention is preferably within the range of -10°C to about 10°C, more preferably from about -5°C to about 5°C. When T_g is lower than -10°C, preadhesion (tack) tends to become excessively high, and when T_g exceeds 10°C, on the contrary, preadhesion tends to become too low. Furthermore, T_g values in these preferred ranges allow the adhesive to possess good peel strength even after absorption of monomeric plasticizer from the PVC component.

The term "glass transition temperature" (T_g) of adhesives useful in the invention means a measurement value determined through the use of dynamic mechanical analysis (DMA) using a Bohlin VOR rheometer. For each adhesive sample, the oscillation experiment yielded the storage (G') and loss shear relaxation moduli (G") as a function of frequency and temperature. The parallel plates used were 1 inch (2.54 cm) in diameter. The thickness of the adhesive samples ranged from 0.5 to 2 mm. For each sample tested, the first set of measurements were taken at 25°C. Using liquid nitrogen, measurements were taken starting at 10°C down to -40°C at 10° increments. There was roughly a 15 minute interval between measurements at different temperatures to allow the adhesive sample to relax and attain equilibrium at the set temperature. At each temperature, the frequency sweeps ranged from 0.063 to 63 rad/sec. The normal force was held constant and the torque was about 20 gm-cm. For every sample, G' and G" were obtained at each temperature. The ratio (G"/G'), a unitless parameter typically denoted "tan δ", was plotted versus temperature. The maximum point (point where the slope was

zero) in the transiti n region between the glassy region and the rubbery region f the tan δ curve, if well defined, determined the T_g of the adhesive.

H. Polymerization Methods

Adhesives useful in the invention can be polymerized by conventional free radical polymerization methods, whether thermally or radiation initiated, including solution and bulk polymerization processes.

In one solution polymerization method, the acrylate ester component, basic copolymerizable component and acidic polar component along with a suitable inert organic solvent and free radically copolymerizable crosslinker are charged into a four-neck reaction vessel which is equipped with a stirrer, a thermometer, a condenser, addition funnel and a thermowatch. After this monomer mixture is charged into the reaction vessel, a concentrated thermal free radical initiator solution is added to the addition funnel. The whole reaction vessel and addition funnel and their contents are then purged with nitrogen to create an inert atmosphere. Once purged, the solution within the vessel is heated to about 55°C, the initiator is added, and the mixture is stirred during the course of the reaction. A 98 to 99 percent conversion should be obtained in about 20 hours.

Another polymerization method is a two step ultraviolet (UV) radiation initiated photopolymerization of a 100% solids monomer mixture. In the first step, the low viscosity monomers are mixed at the appropriate ratios and a photoinitiator is added to the mixture. The mixture is purged with nitrogen to remove dissolved oxygen. Short exposure to UV light results in a partially polymerized syrup with moderate viscosity that can be coated easily. Further photoinitiator and crosslinker are added to the syrup. The syrup is then coated (while excluding O_2) at a desired thickness, usually about 0.5 to 10 mils (about 0.01 to 0.25 millimeters). During the coating process, the syrup is further exposed to a bank of UV lights to complete the polymerization and crosslink the adhesive.

An alternative to the above two step method involves the use of an extruder. In this method, a plastic pouch is filled with monomers and initiators, with the addition of chain transfer agents to keep the molecular weight low enough after polymerization so that the polymer can be extruded. The filled pouch is exposed to UV, which produces the polymerized composition inside the pouch. The pouch and contents are then fed to the extruder and the resulting molten composition hot melt coated onto a liner, after which it is then exposed again to UV or electron beam to crosslink the adhesive, to yield a composition comprising a high moloecular weight PSA having a small percentage of pouch plastic polymer material therein, typically 3 weight percent or less.

Reactive extrusion, such as the continuous free radical polymerization methods described in U.S. Pat. Nos. 4,619,979 and 4,843,134 (both Kotnour et al.), may also be utilized to prepare PSAs useful in the invention. Reactive extrusion is a solventless technology where the polymerization is initiated by thermal means as opposed to UV radiation. The monomers along with the initiator are fed to an extruder. The temperature along the extruder is varied to control the polymerization. Chain transfer agents are added to control the molecular weight and prevent gel formation. The adhesive obtained at the end of the extruder is hot melt coated and cured either by UV light or electron beam in order to improve its cohesive strength..

I. Solvents and Optional Adhesive Ingredients

Suitable inert organic solvent, if required, may be any organic liquid which is essentially inert to the reactants and product and will not otherwise adversely affect the reaction. Such solvents include ethyl acetate, acetone, methyl ethyl ketones, and mixtures thereof. The amount of solvent is generally about 30-80% by weight based on the total weight of the reactants (monomer, crosslinker, initiator) and solvent.

Other useful materials which can be blended into the pressure-sensitive adhesive layer include, but are not limited to those selected from the group

consisting of fillers, pigments, woven and nonwoven fabrics, antioxidants, stabilizers, fire retardants, and viscosity adjusting agents.

PVC Components

There are many types of monomericly plasticized PVC component materials, including: PVC coated fabric; vinyl films containing as much as 25 to 100 parts of monomeric plasticizer (usually dioctylphthalate) to 100 parts vinyl resin; and vinyl coated papers and scrims. Other substrates include PVC substrates such as those mentioned in Japanese published Kokai Nos. 5-263055, 5-140523 and 5-105857, incorporated by reference herein. The '055 publication describes soft vinyl chloride resins containing a metal type stabilizing agent, while the '523 publication describes soft vinyl chloride resins containing an epoxy radical. The '587 publication describes plasticized PVC, wherein the plasticizer is one or more of those listed below.

The primary component of monomericly plasticized PVC coated fabric is of course polyvinyl chloride. Some PVC coated fabrics have an acrylate or methacrylate copolymer added to PVC. The PVC coated fabrics primarily differ in the type and amount of plasticizer added to the polyvinyl chloride. They may also differ in their weight; the most common PVC coated fabric is an 18 oz. per sq. yd. version (610 grams per sq. meter or "gsm"), with the base fabric (usually woven nylon, polyester, or weft inserted fabric) generally weighing from about 5 to about 10 oz. per sq. yd. (about 170 to about 340 gsm), more typically from about 5 oz. per sq. yd. to about 7 oz. per sq. yd. (about 170 to about 240 gsm). The heavier base fabrics are used in heavyweight truck tarpaulins, which may have a weight of up to 25 oz. per sq. yd. (about 850 gsm). Lighter weight fabrics in the 1 oz. to 14 oz. per sq. yd range (about 30 to about 475 gsm) are also within the invention, and are used in applications where weight is important and other physical properties, such as abrasion resistance, are not as important.

As stated previously, both truck covers and tarpaulins are within the invention, including mesh type truck covers, which are light in weight, generally about 5 to about 10 oz. per sq. yd. (about 170 to about 340 gsm).

A study identified the PVC canvas known under the trade designation DURASKIN, style no. B156035, available from Verseidag-Indutex GmbH, Krefeld, Germany as having a high percentage of monomeric plasticizer. A GC and IR analysis of this blue-colored PVC coated fabric revealed that the PVC coating contained about 40 weight percent monomeric plasticizer.

It is theorized that highly monomericly plasticized PVC component materials may contain one or more of the following monomeric plasticizers: phthalic acid derivatives such as dimethyl phthalate, dibutyl phthalate, diethyl phthalate, diheptyl phthalate, di 2-ethylhexyl phthalate, diisooctyl phthalate, di n-octyl phthalate, dinonyl phthalate, diisononyl phthalate, diisodecyl phthalate, diundecyl phthalate, dilauryl phthalate, ditridecyl phthalate, diisobutyl phthalate, dibenzyl phthalate, butylbenzyl phthalate, dicyclohexyl phthalate, dimethoxyethyl phthalate, dibutoxyethyl phthalate, dimethylcyclohexyl phthalate, octyldecyl phthalate, octylbenzyl phthalate, n-hexyl n-decyl phthalate, n-octyl n-decyl phthalate; phthalic isomeride series such as dimethyl isophthalate, dioctyl isophthalate, di 2-ethylhexyl terephthalate; tetrahydrophthalic acid derivatives such as di 2-ethylhexyl tetrahydrophthalate, di n-octyltetrahydrophthalate; phosphoric acid derivatives such as tricresyl phosphate, trioctyl phosphate, triphenyl phosphate, octyldiphenyl phosphate, cresyldiphenyl phosphate, trichloroethyl phosphate, bisphenol A diphenyl phosphate, bisphenol A dixylenyl phosphate; adipic acid derivatives such as dimethyl adipate, dibutyl adipate, diisodecyl adipate, diisobutyl adipate, diisononyl adipate, di 2-ethylhexyl adipate, di n-octyl adipate, didecyl adipate, n-octyl n-decyl adipate, n-hepthyl n-nonyl adipate, benzyloctyl adipate, dibutyldiglycol adipate; sebacic acid derivatives such as di n-butyl sebacate, di n-octyl sebacate, diisooctyl sebacate, di 2-ethylhexyl sebacate, butylbenzyl sebacate; azaleic acid derivatives such as di 2-ethylhexyl azelate, di n-hexyl azelate, dimethyl azelate, dibenzyl azelate, dibutoxyethyl azelate, diisooctyl azelate; citric acid derivatives such as triethyl

citrate, acetyltriethyl citrate, tributyl citrate, acetyltributyl citrate, acetyltrioctyl citrate; epoxy derivatives such as epoxidified soybean oil; polyesters such as polypropylene adipate, polypropylene sebacate; chlorinated materials such as chlorinated paraffin and chlorinated fatty acid ester; glycolic acid derivatives such as methylphthalyl ethylglycolate, ethylphthalyl ethylglycolate, and butylphthalyl butylglycolate; trimellitic acid derivatives such as tri 2-ethylhexyl trimellitate and tri n-octyl n-decyl trimellitate; ricinoleic acid derivatives such as methylacetyl ricinolate and butylacetyl ricinolate; butyloleate; petroleum resin mineral oils such as paraffin series process oils, aromatic series process oils, specialized process oil, ethylene and α-olefin oligomer, paraffin wax, fluid paraffin, white oil, petrolatum, petroleum sulfonic acid, petroleum sulfonate, petroleum asphalt, and petroleum resin; vegetable oils such as castor oil, cottonseed oil, soybean oil, coconut oil, peanut oil, Japan wax rosin, pine oil, dipentene, pine tar softener, tall oil, purified tall oil; aliphatic acid and aliphatic acid salts such as ricinoleic acid, palmic acid, barium stearate, calcium stearate, magnesium stearate, and zinc stearate. Among these compounds, one or more can be used. These plasticizers are generally used in weight percentages ranging from about 10 to 50 percent by weight of the total weight of PVC coated fabric.

It is theorized that retroreflective sheeting may be effectively adhered to materials other than plasticized PVC canvas using the adhesives of the invention, such as polyvinylidene chloride, polyvinyl acetate, polystyrene, PMMA, polyacetyl, polycarbonate, polyamide, acetylcellulose, fluoroplastic, automotive paints, and the like.

Examples and Test Methods

The invention will be described more concretely with reference to the following nonlimiting examples and test methods. All parts, percentages, and ratios are by weight unless otherwise specified.

Abbreviati ns and Trade names

EA	ethyl acrylate
EHA	2-ethyl hexyl acrylate
CA 2	an acrylic solvent based adhesive known under the trade designation AEROSET 1845, from Ashland Chemical Co., Columbus, OH.
CA 3	an adhesive comprising 93/7 IOA/AA crosslinked with N,N'-bis-1,2-propyleneisophthalamide
CA 4	an adhesive blend of 65% of an acrylic latex (80/16/4 EA/BA/AA) and 35% of a urethane latex known under the trade designation BAYBOND 402a thickened with a thickener known under the trade designation QR0708, from Rohm and Haas, as generally described in Examples 1-8 of U.S. Pat. No. 5,229,207
CA 5	a acrylic transfer adhesive known under the trade designation 9465, available from 3M, comprising IOA/NVP/AA with diisononyl phthalate (DINP) plasticizer, as described in U.S. Pat. No. 4,985,488.
IBA	isobornyl acrylate
KB-1	benzildimethylketal, available from Sartomer under the trade designation ESCACURE KB-1
AA	acrylic acid
BA	n-butyl acrylate
IOA	isooctyl acrylate
HDDA	1,6-hexanediol diacrylate
hr.	hour

min.	minutes
NNDMA	N,N-dimethyl acrylamide
R.T.	room temperature (about 20-25°C)
PVC/CF	the PVC coated fabric known under the trade designation DURASKIN, style no. B 156035
ABP	4-acryloxybenzophenone
ANT	anthraquinone
CPIA	an acrylamido functional disubstituted acetyl aryl ketone

Test Methods

Static Shear Test

This test is conducted in accordance with PSTC-7, a procedure specified in "Test methods for Pressure-Sensitive Tapes," 8th edition, available from the Pressure-Sensitive Tape Council, Glenview, IL., U.S.A. A 12.7 mm X 10cm strip of the adhesive to be tested was applied to a sealing film. This was placed on a vertical PVC coated fabric test panel so that 12.7 mm X 25.4 mm of adhesive is in contact. A hand roller was used to establish good contact between the adhesive, sealing film and PVC coated fabric test panel. These samples were conditioned in a constant temperature (R.T.) and relative humidity (about 50%) (CTRH) room for 24 hrs. At this stage, a 1 kg load was attached to a free end f the sealing film and the time to failure was noted. The samples that failed were examined for the mode of failure. The test is typically used to determine the cohesive strength of the adhesive under shear at room temperature. However, if the adhesion to the substrate or backing is poor or the adhesive is over/cross-linked, the failure is adhesive in nature. If no failure had occurred in 10,000 minutes, the test was discontinued. In addition, the samples were thermally

conditioned at 158° F (70°C) for 1 week and tested for their shear performance at room temperature using the same procedure.

Pressure Wash Test

This test was in accordance with a General Motors Standard No.9531P, March 1989, to test the ability of a conspicuity sheeting to withstand high pressure car wash spray. A 25.4 mm X 50.8 mm strip of the adhesive was laminated to the sealing film of a cube-corner retroreflective sheeting and this was applied to a PVC coated fabric test sample. A hand roller was used to establish good contact between the adhesive and the PVC coated fabric. The samples were conditioned in a constant temperature and relative humidity (about 50%) (CTRH) room for 24 hrs. Half of the samples were placed in an oven for thermal conditioning at 158° F (70°C) for 1 week and the other half in a distilled water bath at R.T. for 10 days. Upon removal, the samples were placed in a fixture such that the bottom of the sheeting was 212 mm away from a R.T. or cooler water spray nozzle and the top was tilted at a 45° angle away from the water spray. The water spray was directed at the base of the sheeting for 15 seconds at a pressure of around 8500 kPa. At the end of the test, the sheeting bottom was evaluated for lifting away from the PVC. If the lifting was less than 1 mm, it was assigned a pass rating. The article was judged to have failed the pressure wash test if the sheeting lifted greater than 1 mm uniformly.

T-peel Test

A 25.4 mm X 152.4 mm strip of adhesive was laminated to the sealing film of a cube-corner retroreflective sheeting and this was applied in partial overlapping fashion to a similar sized PVC coated fabric such that an end portion of the PVC coated fabric was free of adhesive. A hand roller was used to establish good contact between the adhesive, the sealing film and the PVC coated fabric. The samples were conditioned in a constant temperature (R.T.) and relative humidity (50%) (CTRH) room for 24 hrs. The sheeting-adhesive-PVC

coated fabric sandwich is termed the composite. The following peel tests were performed to test the adhesive performance:

a) Peel after the 24 hour dwell in the CTRH;

b) Peel after thermal conditioning by placing the composite in an oven at 158° F (70°C) for 1 week;

c) Peel after placing the composite in a distilled water bath at R.T. for 10 days.

After conditioning, the composite was placed in a tensile testing machine known under the trade designation SINTECH such that the end of the sheeting with the adhesive was clamped in the upper jaw and the end comprised only of PVC coated fabric was clamped in the lower jaw. The jaws were then separated at 30.5 cm/minute and the force required to effect the separation was noted in lb_f/in. The original adhesive thickness was 0.127 mm.

Examples

Examples 1-4 and Comparative Examples C-1 - C-5

Example 1

A mixture of 80 parts IOA, 15 parts of the moderately basic copolymerizable monomer NNDMA, 5 parts AA, 0.10 part KB-1 was inerted and partially photopolymerized under ultraviolet (UV) irradiation (40 watt fluorescent black lamp having 90% of the emissions between 300 and 400 nm and a maximum at 351 nm and which provides radiation intensity of about 1-2 mW/cm^2) to yield a coatable syrup of about 3,000 centipoise (cPs). Then 0.1 part of KB-1 and 0.08 part HDDA were added to the syrup with thorough mixing. The sample was coated at 127 micrometer thickness between two siliconized polyester liners and polymerized under a bank of the same fluorescent UV lamps. The total UV dose was about 300 mJ/cm^2, which yielded a pressure-sensitive adhesive. Test samples were prepared as explained in Test Methods. The substrate was a dual layered film comprising a 2.5 mil (0.64 mm)

polyurethan layer and a 4 mil (1.0 mm) polycarbonate reinforcement layer, with the polyurethane layer facing the adhesive.

The results of the tests for Examples 1-4 and Comparative Examples C-1, C-2, C-3, C-4, and C-5can be found in Table 1.

Example 2

A test sample was made and tested as in Example 1, except the adhesive used had a ratio of 80 parts IOA, 18 parts NNDMA, 2 parts AA, and 0.08 part HDDA was used.

Example 3

A test sample was made and tested as in Example 1, except the adhesive used had a ratio of 80 parts BA, 18 parts NNDMA, 2 parts AA, and 0.08 part HDDA.

Example 4

A test sample was made and tested as in Example 1, except the adhesive used had a ratio of 60 parts IOA, 25 parts IBA, 15 parts NNDMA, and 0.08 part HDDA.

Comparative Example C-1

A test sample was made as in Example 1, except the adhesive used had a ratio of 65 parts IOA, 33 parts IBA and 2 parts acrylic acid (AA), which is termed CA 1 in Table 1.

Comparative Example C-2

For this comparative example, a test sample was made as in Example 1, except the adhesive used was CA 2.

Comparativ Example C-3

For this comparative example, a test sample was made as in Example 1, except th adhesive used was CA 3.

Comparative Example C-4

For this comparative example, a test sample was made and tested as in Example 1, except the adhesive used was CA 4.

Comparative Example C-5

For this comparative example, a test sample was made and tested as in Example 1, except the adhesive used was CA 5.

Table 1

Ex.	Comp.	T-Peel (N/cm)[1]	T-Peel (lb_f/in)[1]	T_g (°C)
1	IOA/NNDMA/AA/HDDA	12.1, 5.8, 4.9	6.9,3.3,2.8	-3
2	IOA/NNDMA/AA/HDDA	9.3, 5.1, 6.1	5.3, 2.9, 3.5	-14
3	BA/NNDMA/AA/HDDA	11.9. 5.6, 7.0	6.8, 3.2, 4.0	-13
4	IOA/IBA/NNDMA/HDDA	7.4, 5.1, 6.5	4.2, 2.9, 3.7	0
CA-1	IOA/IBA/AA/HDDA	7.2, 0.7, 6.5	4.1, 0.4, 3.7	-8
CA-2	AEROSET 1845	10.5, 1.8, 8.6	6.0, 1.0, 4.9	-35
CA-3	IOA/AA	4.0, 0.5, 1.9	2.3, 0.3, 1.1	--
CA-4	65% of an acrylic latex (80/16/4 EA/BA/AA) and 35% of a urethane latex	3.0, 4.9, 0.7	1.7, 2.8, 0.4	--
CA-5	IOA/NVP/AA/DINP	4.7, 3.5, 3.3	2.7, 2.0, 1.9	-4

[1] Peel Force (initial, 7 day oven, 10 day water soak)

Peel values less than 2 lb_f/in (3.5 N/cm) were considered unacceptable and values greater than 3 lb_f/in (5.3 N/cm) were preferred. The CA-3 and CA-4 adhesives gave unacceptable performance in at least two of the three T-peel tests. The CA-5 adhesive gave values close to the unacceptable range in both the thermal conditioned and water soak T-peel test.

The CA-1 and CA-2 adhesives exhibited high initial and 10 day water soak T-peel values but performed poorly in the T-peel test after thermal conditioning. The adhesive probably absorbed the plasticizer during thermal conditioning, and as a result, its performance was lowered.

In addition, the adhesives of comparative Examples CA-1, CA-2, CA-3, CA-4, and CA-5 all failed the pressure wash test after thermal conditioning.

In contrast, the preferred inventive adhesive of Example 1 exhibited acceptable T-peel values in all the tests. The initial adhesion was high (~ 6.9 lb_f/in [12.1 N/cm]). The values dropped after both thermal conditioning and water soaking but the peel values in both these tests were a significant improvement over the Comparative Examples. Further, this adhesive passed th pressure wash test after both thermal conditioning and water soaking.

At comparable T_g's, the 60/25/15 IOA/IBA/NNDMA formulation (Example 4) exhibited lower initial and thermal conditioned peel values than the 80/15/5 IOA/NNDMA/AA formulation of Example 1. However, the adhesive of Example 4 exhibited 10 day water soak peel values not much lower than the 24 hr. R.T. dwell peels. The absence of AA and the presence of the hydrophobic acrylate, IBA, helped the adhesive maintain its performance after immersing in water. This and all the IOA/NNDMA/AA formulations passed both the thermal conditioned and water soak pressure wash tests.

In addition, it should be noted that the adhesive of Example 3 exhibited better T-peel results than the adhesive of Example 2.

Examples 5-9

Example 5

A premix was prepared using 80 parts IOA, 15 parts NNDMA, 5 parts AA, and 0.04 part KB-1. This mixture was partially polymerized under a nitrogen-rich atmosphere by exposure to ultraviolet radiation (40 watt black lamp) to provide a coatable syrup having a viscosity of about 3000 cps. 0.05 part HDDA and 0.16 part KB-1 were then added to the syrup and it was knife

coated onto silicone-treated polyethylen -coated paper release liner at a thickness of 5 mils (0.127 mm). The resulting composite was then exposed to ultraviolet radiation having a spectral output from 300-400 nm with a maximum at 351 nm in a nitrogen-rich environment. An intensity of about 3 mW/cm^2 was used during an exposure time sufficient to result in a total energy of 550 mJ/cm^2.

The adhesives of Examples 5-9 were tested in accordance with the test methods above and the results shown in Table 2.

Example 6

A test sample was made and tested as in Example 5, except that 0.075 part ABP was added prior to the partial polymerization step, and 0.04 part of HDDA rather than 0.05 part was added to the syrup.

Example 7

A sample was made and tested as in Example 5, except that 0.108 part of ABP was substituted for the HDDA, an intensity of about 3 mW/cm^2 was used during an exposure time sufficient to result in a total energy of 450 mJ/cm^2 in a first curing step, and a second high intensity UV curing step was used which employed a medium pressure mercury vapor lamp for a time sufficient to produce a total energy in the second step of 250 mJ/cm^2.

Example 8

A sample was made and tested as in Example 7, except that 0.09 part of ANT was substituted for the ABP.

Example 9

A sample was made and tested as in Example 7, except that 0.3 part of CPIA was substituted for the ABP.

Table 2

Ex.	Comp.	Amounts	T-Peel (N/cm)[1]	T-Peel (lb_f/in)[1]
5	IOA/NNDMA/AA/HDDA / KB-1	80/15/5/0.05/0.2	11.1, 6.3, 3.6	6.3, 3.6, 3.6
6	IOA/NNDMA/AA/HDDA /ABP/KB-1	80/15/5/0.04/0.075 / 0.2	12.6, 7.4, 7.7	7.2, 4.2, 4.4
7	IOA/NNDMA/AA/ABP/ KB-1	80/15/5/0.108/0.2	13.3, 7.0, 8.4	7.6, 4.0, 4.8
8	IOA/NNDMA/AA/ANT/ KB-1	80/15/5/0.09/0.2	13.1, 7.2, 9.3	7.5, 4.1, 5.3
9	IOA/NNDMA/AA/CPIA/ KB-1	80/15/5/0.3/0.2	11.9, 8.8, 8.1	6.8, 5.0, 4.6

[1] Peel Force (initial, 7 day oven, 10 day water soak)

All articles of the invention made using the adhesives of Examples 5-9 passed the static shear test and exhibited acceptable T-peel values in all the tests. The initial adhesion was high for all of these examples. The values dropped on both thermal conditioning and water soaking but the peel values in both these tests were a significant improvement over the Comparative Examples of Table 1. Further, the adhesives of Examples 5-9 passed individual pressure wash tests after thermal conditioning and water soaking.

In summary, adhesive formulations based on IOA/NNDMA/AA and BA/NNDMA/AA adhesives, the 80/18/2 BA/NNDMA/AA formulation and the 80/15/5 IOA/NNDMA/AA adhesive are particularly preferred for use in the inventive articles.

Further modifications to the adhesives and articles of the invention will be apparent to those having skill in the art. Thus, the appended claims are not limited to their literal wording nor to the specifically described embodiments.

CLAIMS:

1. An article comprising:

(a) a layer of pressure-sensitive adhesive comprising a crosslinked copolymer of 100 parts by weight monomer of elements (i), (ii), (iii) and optionally (iv) characterized in that the copolymer comprises:

(i) about 50 to about 90 parts by weight of at least one monomer selected from the group consisting of a first monofunctional acrylate or methacrylate ester of a non-tertiary alkyl alcohol, and mixtures thereof, the alkyl group of which comprise from about 4 to about 12 carbon atoms, which as a homopolymer has a glass transition temperatures less than -25°C;

(ii) about 10 to about 25 parts by weight of a moderately basic copolymerizable monomer selected from the group consisting of N,N-dialkyl substituted amides;

(iii) about 0 to about 7 parts by weight of an acidic monomer copolymerizable with the monomers of elements (i) and (ii), wherein when the acidic monomer is included, the basic copolymerizable monomer is present in a molar excess;

(iv) 0 to about 30 parts by weight of a second monofunctional acrylate or methacrylate ester of a non-tertiary alcohol having as a homopolymer a glass transition temperature equal to or greater than -25°C; and

(v) about 0.01 to about 1 percent by weight of a crosslinking agent based upon the total weight of (i) plus (ii) plus (iii) plus (iv), wherein the relative amounts of the monomers are selected such that the article passes at least three tests selected from the group consisting of a pressure wash test after water soaking, a pressure wash test after thermal conditioning, a static shear test (initial), a static shear test after thermal conditioning, a T-peel test (initial), a T-peel test after thermal

conditioning, and a T-peel test after water soaking; and
(b) a substrate onto which the adhesive is coated.

2. . Article in accordance with claim 1 further characterized in that a highly monomericly plasticized PVC component having at least one surface is adhered with the pressure-sensitive adhesive to the substrate.

3. Article in accordance with claim 2 further characterized in that said substrate is selected from the group consisting of i) a transparent retroreflective sheeting having a substantially flat surface and a structured second surface, the structured second surface comprised of a plurality of grooves defining a plurality of peaks, a polymeric sealing film attached to the structured second surface at a plurality of locations, the sealing film contacting said adhesive, ii) a metallized retroreflective sheeting having a substantially flat surface and structured second surface, the structured surface having a layer of metal thereon, the adhesive contacting the metal layer, iii) the non-light-impinging surface of a beaded retroreflective sheeting , and iv) non-retroreflective substrates selected from the group consisting of polymeric films and soft metallic films.

4. Article in accordance with claim 2 further characterized in that said highly monomericly plasticized PVC component is a highly monomericly plasticized PVC coated fabric.

5. Article in accordance with claim 4 further characterized in that the PVC component comprises from 10 to about 50 weight percent monomeric plasticizer.

6. Article in accordance with claim 1 further characterized in that said N,N-dialkyl substituted amide is selected from N-vinyl pyrrolidone, N-vinyl caprolactam, and monomers within the general formula (I):

$$\begin{array}{c} R \\ | \\ CH_2{=}C\text{-}Z \end{array} \qquad (I)$$

wherein:

R is selected from the group consisting of -H and $-CH_3$;

Z is -C (=O)NR^1R^2; and

R^1 and R^2 are independently selected from the group consisting of alkyl groups having from 1 to 10 carbon atoms.

7. The article of claim 1 further characterized in that the first monofunctional acrylate ester monomer is selected from the group consisting of n-butyl acrylate, n-butyl methacrylate, isobutyl acrylate, 2-methyl butyl acrylate, 2-ethylhexyl acrylate, n-octyl acrylate, isooctyl acrylate, isooctyl methacrylate, isononyl acrylate, isodecyl acrylate, and mixtures thereof.

8. The article of claim 1 further characterized in at least one of the following:

a) said moderately basic copolymerizable monomer about 14 to about 20 parts by weight; or

b) the acidic monomer is present at from about 3 to about 6 parts by weight; or

c) said second monofunctional acrylate ester is present at from about 1 to about 30 parts by weight.

9. The article of claim 8 further characterized in that the moderately basic copolymerizable monomer is selected from the group consisting of N,N-dimethyl acrylamide, N,N-dimethyl methacrylamide, N,N-diethyl acrylamide, N,N-diethyl methacrylamide and mixtures thereof.

10. The article of claim 1 further characterized in that the acidic monomer is selected from the group consisting of ethylenically unsaturated carboxylic acids, ethylenically unsaturated sulfonic acids, ethylenically unsaturated phosphoric acids, and mixtures thereof.

11. The article of claim 10 further characterized in that the acidic monomer is selected from the group consisting of acrylic acid, methacrylic acid, itaconic acid, fumaric acid, crotonic acid, citraconic acid, maleic acid, β-carboxyethyl acrylate, sulfoethyl methacrylate, and mixtures thereof.

12. The article of claim 1 further characterized in that the crosslinking agent is selected from the group consisting of multifunctional acrylates, substituted triazines, mono-ethylenically unsaturated silanes, hydrogen abstraction compounds, copolymerizable α-cleavage type photoinitiators, bisamide compounds, and heat activated copolymerizable crosslinking agents.

13. A method of bonding a highly monomericly plasticized PVC component to a substrate, characterized in that the method comprises the steps of:

(a) formulating a pressure-sensitive adhesive composition comprising a crosslinked copolymer of 100 parts by weight monomer of elements (i), (ii), (iii) and optionally (iv) wherein the copolymer comprises:

(i) about 50 to about 90 parts by weight of at least one monomer selected from the group consisting of a first monofunctional acrylate or methacrylate ester of a non-tertiary alkyl alcohol, and mixtures thereof, the alkyl group of which comprises from about 4 to about 12 carbon atoms, which as a homopolymer has a glass transition temperature less than -25°C;

(ii) about 10 to about 25 parts by weight of a moderately basic copolymerizable monomer selected from the group consisting of N,N-dialkyl substituted amides;

(iii) about 0 to about 7 parts by weight of an acidic monomer copolymerizable with the monomers of elements (i) and (ii), wherein when the acidic monomer is included, the basic copolymerizable monomer is present in a molar excess;

(iv) 0 to about 30 parts by weight of a second monofunctional acrylate ester of a non-tertiary alcohol having as a homopolymer a glass transition temperature equal to or greater than -25°C; and

(v) about 0.01 to about 1 percent by weight of a crosslinking agent based upon the total weight of (i) plus (ii) plus (iii) plus (iv),

(b) applying the adhesive composition either to a highly monomericly plasticized PVC component, a surface of a substrate, or both; and

(c) joining the substrate with the PVC component, the adhesive composition disposed between the PVC component and the material forming said surface of the substrate.

14. Method in accordance with claim 13 further characterized in that said substrate is selected from the group consisting of i) a transparent retroreflective sheeting having a substantially flat surface and a structured second surface, the structured second surface comprised of a plurality of grooves defining a plurality of peaks, a polymeric sealing film attached to the structured second surface at a plurality of locations, the sealing film contacting said adhesive, ii) a metallized retroreflective sheeting having a substantially flat surface and structured second surface, the structured surface having a layer of metal thereon, the adhesive contacting the metal layer, iii) the non-light-impinging surface of a beaded retroreflective sheeting , and iv) non-retroreflective substrates selected from the group consisting of polymeric films and soft metallic films.

15. Method in accordance with claim 13 further characterized in that the acidic monomer is present at from about 3 to about 6 parts by weight, and the moderately basic monomer is present at from about 14 to about 20 parts by weight.

16. Method in accordance with claim 13 further characterized in that the moderately basic monomer is selected from the group consisting of N,N-dimethyl acrylamide, N,N-dimethyl methacrylamide, N,N-diethyl acrylamide, N,N-diethyl methacrylamide and mixtures thereof.

17. Method in accordance with claim 13 further characterized in that after step (b) and prior to step (c) the adhesive is exposed to conditions sufficient to crosslinked the adhesive.

18. Method in accordance with claim 22 wherein said conditions comprise the step of exposing the adhesive to an electron beam.

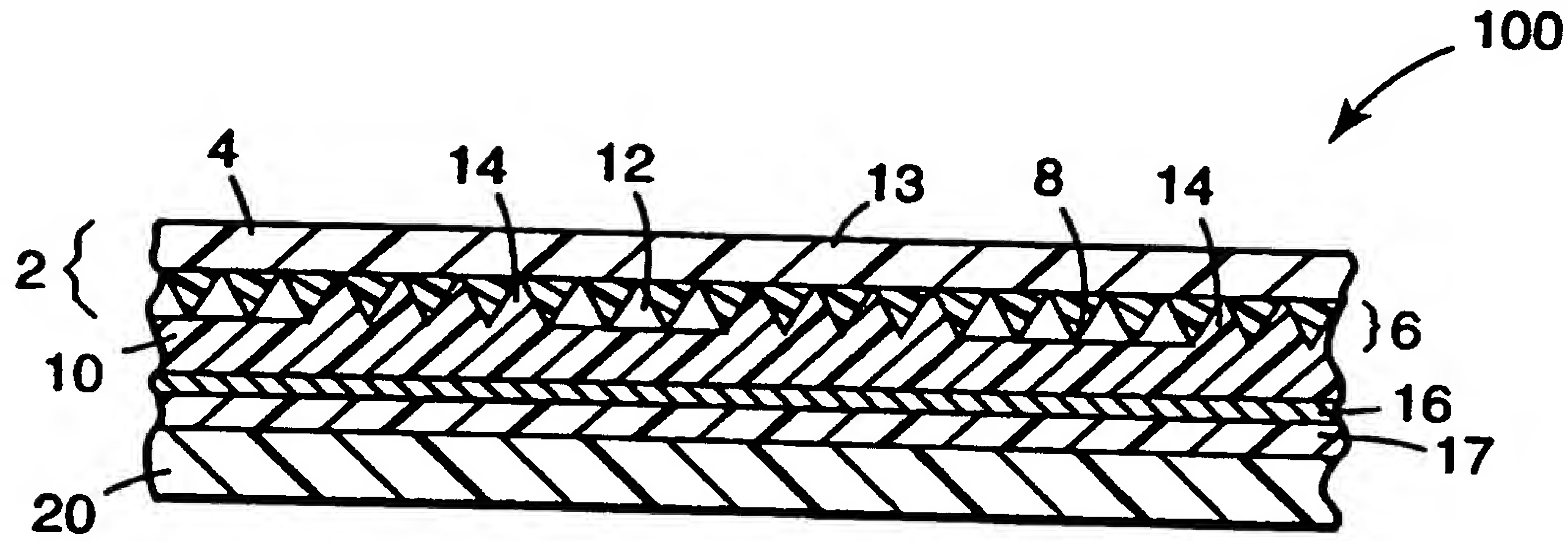


Fig.1

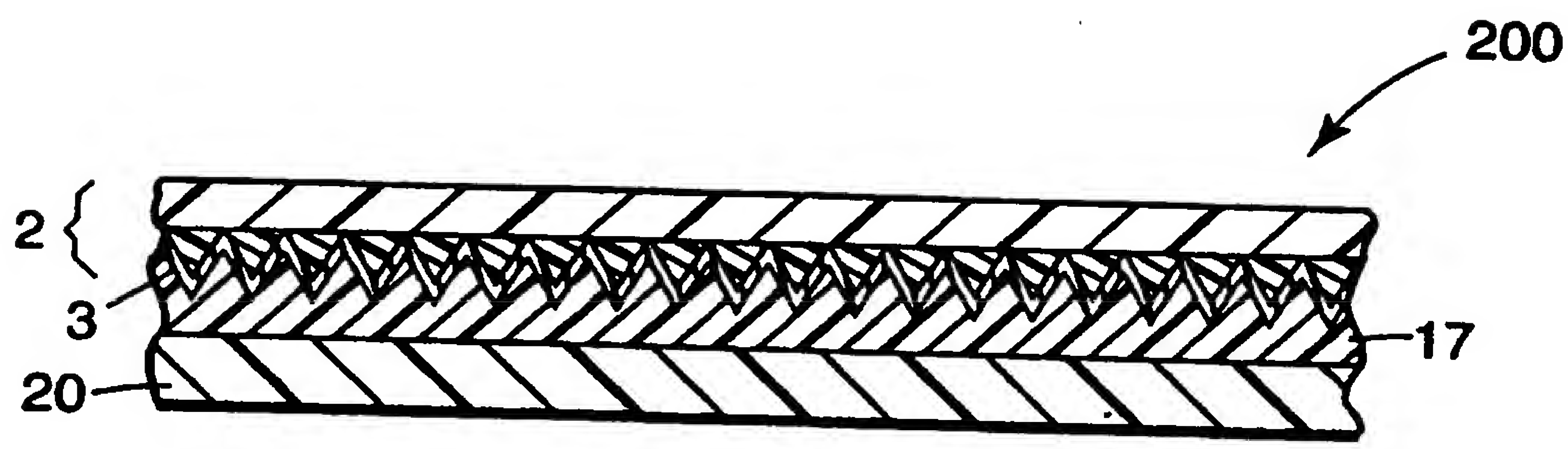


Fig.2

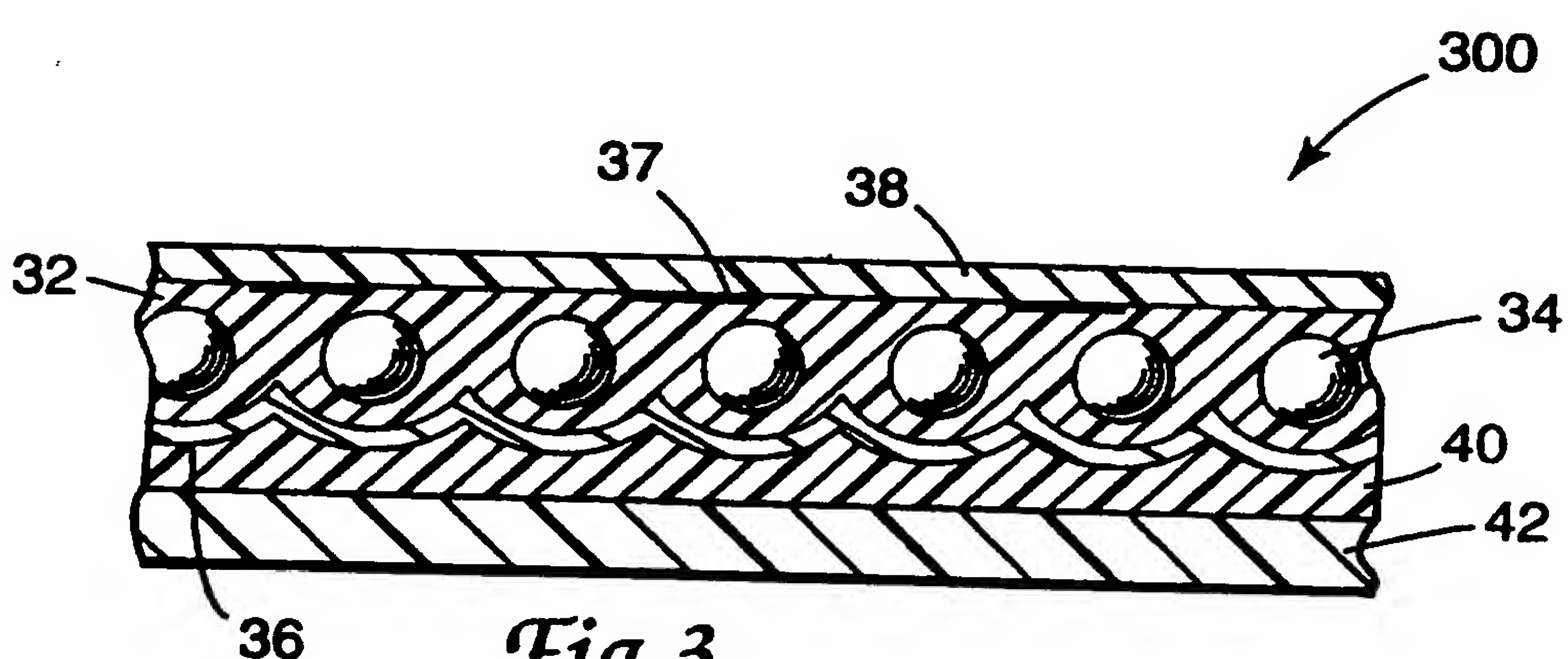


Fig.3